ZERO GAS REFERENCE STANDARDS

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CITAC Best Paper Award 2016
Introduction

- EMRP MacPoll Project

Goal:
Improve the traceability and comparability of measurement results of current air monitoring techniques
What is “zero gas”?

Air or N₂ with a specification for relevant impurities to meet the requirements of European air quality standards for the reference methods used to measure pollutants in air.

More generally, zero gas is usually a high purity source of the matrix gas being measured, where components of relevance to the measurements are present at negligible amount fractions or are quantified so as to not cause a systematic bias.
Introduction

- Is there a universal “zero gas”?

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<table>
<thead>
<tr>
<th>Impurity</th>
<th>SO$_2$</th>
<th>NO/NO$_2$</th>
<th>O$_3$</th>
<th>CO</th>
<th>SO$_2$</th>
<th>NO/NO$_2$</th>
<th>O$_3$</th>
<th>CO</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>≤4000</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>≤4000</td>
</tr>
<tr>
<td>O$_3$</td>
<td>—</td>
<td>≤2</td>
<td>≤1</td>
<td>—</td>
<td>—</td>
<td>≤2</td>
<td>≤1</td>
<td>—</td>
</tr>
<tr>
<td>H$_2$S</td>
<td>≤100</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>≤2</td>
<td>≤1</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>≤10</td>
<td>≤10</td>
<td>—</td>
</tr>
<tr>
<td>NO</td>
<td>≤1</td>
<td>≤1</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>≤1</td>
<td>≤1</td>
<td>—</td>
</tr>
<tr>
<td>NO$_2$</td>
<td>≤1</td>
<td>≤1</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>≤1</td>
<td>≤1</td>
<td>—</td>
</tr>
<tr>
<td>N$_2$O</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>m-Xylene</td>
<td>≤1</td>
<td>—</td>
<td>≤1 (xylenes)</td>
<td>—</td>
<td>—</td>
<td>— (xylenes)</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Toluene</td>
<td>—</td>
<td>—</td>
<td>≤1</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>≤150 000</td>
<td>≤150 000</td>
<td>≤150 000</td>
<td>≤150 000</td>
<td>≤150 000</td>
<td>≤150 000</td>
<td>≤150 000</td>
<td>≤150 000</td>
</tr>
<tr>
<td>SO$_2$</td>
<td>≤1</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>CO</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>≤100</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>≤100</td>
</tr>
</tbody>
</table>

Table 1 Specifications of the zero gas for type approval of nitrogen monoxide, nitrogen dioxide, sulphur dioxide, ozone and carbon monoxide analysers. Values have been obtained from standards EN 14212 (sulphur dioxide), EN 14211 (nitrogen monoxide and nitrogen dioxide), EN 14625 (ozone) and EN 14626 (carbon monoxide).
Introduction


[Diagram: Describes the problem of zero gas → Describes current solutions → Comparison of generators and purifiers]
Description of the problems

- We need to know the amount of impurities to properly **assess the uncertainty** of measurements.
- Impurities in commercial high purity gases reported as a **maximum value with no uncertainty**.
- Zero air generators and filters degrade with use and time.
  - There are no reference standards for zero gases.
Description of the problems

- How reference gas mixtures are prepared?
Description of the problems

Quantification of target components in balance gases is essential but very challenging due to:

- The **detection limits** of current analytical techniques.
- The difficulty of establishing a **real zero response** against which to compare.
- Moreover, absolute analytical methods also require a zero gas to define the baseline.

**Catch 22 situation**

I can't find a job because I have no experience

I have no experience because I can't find a job

To adjust the zero I need a reference zero gas

To obtain a reference zero gas I need to adjust the zero
Current solutions

Fig. 1  Classification of analytical techniques as a function of their need for calibration and an absolute zero.
Current solutions

- What is currently done at NPL in the field of air quality?

  Standard addition method

Applicable to “relative” analytical techniques
Circular approach
Current solutions

- What is currently done with absolute spectroscopy?

The capability of these techniques depends on:
- Their limits of detections
- Their traceability to the SI

Project EURAMET 934 provided guidelines to underpin a future standard for SI traceability (TILSAM method)

Comparison of generators and filters

- In field, automated analysers of air pollutants are usually zeroed with purified compressed air.

<table>
<thead>
<tr>
<th>ZAG 1</th>
<th>ZAG 2</th>
<th>ZAG 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow (L min⁻¹)</td>
<td>NO (nmol mol⁻¹)</td>
<td>NO₂ (nmol mol⁻¹)</td>
</tr>
<tr>
<td>1–5</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td>1–20</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td>8</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3: Manufacturer specifications for the zero air generators

<table>
<thead>
<tr>
<th>Gases purified</th>
<th>Impurities removed</th>
<th>Outlet amount fraction</th>
<th>Maximum flow rate</th>
<th>Regeneration</th>
</tr>
</thead>
<tbody>
<tr>
<td>PURIFIER 1</td>
<td>Compressed dry air, N₂, O₂, H₂O, CO, CO₂, organics (C &gt; 4), SO₂, NO₃, HCl, H₂S, NH₃ and amines, hydrocarbons with heteroatoms such as Si, halogens, P, B, S, or metals</td>
<td>&lt;1.0 nmol mol⁻¹</td>
<td>50 slpm</td>
<td>In factory</td>
</tr>
<tr>
<td>PURIFIER 2</td>
<td>Compressed dry air, N₂, O₂, He, SO₃/SO₂, H₂S, toluene, CO/CO₂, NH₃, H₂O, acid gases, alcohols, amines, ammonia, hydrocarbons, H₂O, NO₂, siloxanes</td>
<td>&lt;0.5 nmol mol⁻¹</td>
<td>25 slpm</td>
<td>In factory or field</td>
</tr>
</tbody>
</table>
Comparison of generators and filters

- The three air generators tested in this work complied with the requirements of the relevant standards with the exception of one of them for NO$_2$.
- The two purifiers met the manufacturer specifications, except for CO and filter 2. However, output concentrations were below the limits set by the relevant EN standards.
Conclusions

- The availability of zero gas reference standards is primarily limited by the *limits of detection* of current “absolute” analytical methods and their traceability to the SI.
- Methods to quantify target impurities in balance gases using dynamic dilution and metrology grade air or N₂ to zero the analysers has been proved to give good results for air quality applications.
- Performance of zero gas generators and purifiers meets air quality EN standards requirements, but need routine maintenance.
- More demanding applications will require target gas impurities in zero gas to be more precisely determined but this will only be achieve in parallel with the improvement in sensitivity of analytical techniques.
Thank you